

Low-Cost Electrochemical Impedance Spectroscopy System for Corrosion Monitoring of Metallic Antiquities and Works of Art

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Abstract—Electrochemical impedance spectroscopy (EIS) is recognized to be a powerful and noninvasive technique to test the integrity of protective coatings on memorials, but commercial EIS systems are rather costly though versatile devices. This paper describes a low cost and portable EIS system that is based on a compact digital signal processor (DSP) board and embeds the potentiostatic function so that it can be used without requiring an external potentiostat. The software that runs on the DSP is designed to analyze the electrochemical impedance only in a reduced frequency range in order to produce a simple corrosion alert result. The device is equipped with a digital interface and can be connected to a personal computer to carry out a complete frequency analysis and perform a more complex data processing.

Index Terms—Corrosion testing, electrochemical devices, impedance measurement, intelligent systems, signal processing.

I. INTRODUCTION

METALLIC antiquities and works of art suffer from degradation, which depends on the metal and the environment [1]. Despite the great social importance of recovering these antiquities and conserving them in a good state, there is no general agreement on preferential conservation methods for different metals and alloys [2]. Several organic coatings have been proposed in the years to protect the cleaned artifacts; such coatings have to exert a barrier effect against air, acid gases, oxygen, and other aggressive pollutants, whose amount increases more and more in the environment.

A good coating should be durable, resistant to handling, ductile in order to cope with thermal expansion and volume exchanges from mild corrosion, repairable and removable. Unfortunately, most common good coatings, which provide a durable protection, are often difficult to remove in case of necessity and this limits their use on valuable antiquities. An interesting alternative is represented by reversible coatings, such as the wax based ones, but their duration as well as protection efficiency needs to be tested at regular intervals.

Several techniques can be used to carry out these tests as well as to investigate the corrosion conditions of the surface. Examples of techniques [3] include atomic force microscopy

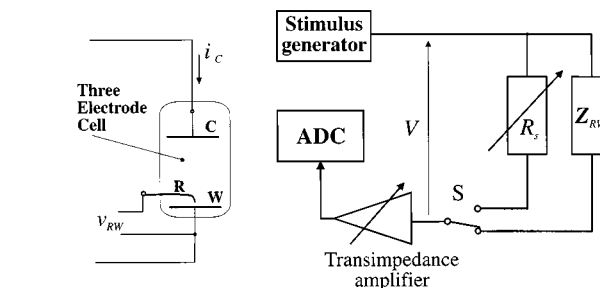


Fig. 1. Three-electrode cell and measurement method.

(AFM), scanning electron microscopy (SEM), x-ray diffraction (XRD), Raman infrared spectroscopy (RIRS), Fourier transform infrared spectroscopy (FTIR), and electrochemical impedance spectroscopy (EIS). Among these techniques, the EIS [4] is the only that can be carried out in the field with compact and portable instruments.

II. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

The electrochemical impedance spectroscopy consists in the measurement of amplitude and phase of the surface impedance of coated metallic objects at different frequencies in order to highlight the barrier properties of the coating. The impedance measurement is carried out by using a three-electrode cell, whose structure is shown in Fig. 1.

The three electrodes are referred to as 1) counter electrode (*C*), 2) reference electrode (*R*), and 3) working electrode (*W*). The impedance is measured between the reference and working electrode and is obtained as the ratio between the voltage v_{RW} and the current i_C that flows through the cell. The measurements have to be carried out by applying a small alternating voltage superimposed to a bias dc voltage between the *C* and *W* electrodes, in order to obtain meaningful results. The applied dc voltage has to be continuously changed in order to maintain a fixed predefined potential difference between the *R* and *W* electrodes.

This is usually obtained by an automatic feedback system, referred to as potentiostat, which continuously monitors the dc voltage between *R* and *W* electrodes and keeps it constant by modifying the dc voltage applied between the *C* and *W* electrodes. The alternating voltage, which is required for the impedance measurement, is also applied between the electrodes *C* and *W*.

Manuscript received May 26, 1999; revised November 19, 1999.

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Publisher Item Identifier S 0018-9456(00)03062-X.

The impedance is typically measured in the frequency range of 1 mHz–100 kHz, while the expected impedance amplitude is in the range of 10 k Ω –10 G Ω , for coated surfaces and cells having an electrode surface of 10 cm².

III. THE PROPOSED LOW-COST EIS SYSTEM

Two are the main constraints which require high quality electric circuits to be employed thus greatly increasing the cost of traditional EIS systems.

The first constraint is related to the wide frequency range traditionally involved in EIS systems, which also requires long measurement sessions to gather the complete impedance spectra.

Fortunately, for the simple monitoring of memorial coatings, a complete spectroscopic analysis can be often avoided, thus limiting the frequency span in the range of 0.1 Hz–10 kHz.

This reduced frequency range appears to be acceptable when the scope of the measurement is to evaluate the protection efficiency of the coating. On the contrary, the need for a very low frequency limit comes when the scope is to obtain kinetic information about the electrochemical processes occurring within the metal/coating/electrolyte system.

The second constraint is connected to the high impedances presented by good coatings. Such high impedances, coupled to the low amplitude of the employed stimulations signals, lead to very small currents through the cell. However, when the simple monitoring of memorial coatings is involved, impedance measurements above 10 M Ω can be carried out with an uncertainty of up to 10% without impairing the instrument performance.

Both the frequency range reduction and the relaxed requirement on the accuracy allow a remarkable cost reduction to be obtained if a proper measurement strategy is employed.

The authors decided to employ a digital approach by converting the involved quantities into numeric samples by means of an Analog to Digital Converter (ADC) and by processing such samples with a time domain algorithm, which is able to greatly reduce both the effects of noise and signal distortion.

In addition, instead of the conventional measurement of voltage and current, the authors employed a substitution measurement method (Fig. 1), in order to directly determine the impedance. The substitution method employs only one ADC, a variable-gain transimpedance amplifier, and a multi-value resistive standard to determine the unknown impedance.

A two-step measurement is performed by acquiring the samples at the output of the transimpedance amplifier when a standard resistor (first step) and the unknown impedance (second step) is connected. The obtained samples are processed by means of the algorithm described in the Appendix thus obtaining two complex numbers M_s and M_u , which are related to the applied voltage V , to the measuring chain gain K , and to the standard and unknown impedances R_s and Z_{RW}

$$M_s = \frac{V}{R_s} K \quad (1)$$

$$M_u = \frac{V}{Z_{RW}} K. \quad (2)$$

The unknown impedance is eventually obtained by means of the ratio between the two measurements:

$$\frac{M_s}{M_u} = \frac{Z_{RW}}{R_s} \frac{VK}{VK} \Rightarrow Z_{RW} = \frac{M_s}{M_u} R_s. \quad (3)$$

Such a substitution method allows a measurement to be performed even though both the applied voltage V and the measuring chain gain K are only roughly known.

The two measurements need not be performed in sequence for each frequency value. A complete set of measurements with the standard resistor is performed before switching to the cell in order to speed up the measurement procedure. This measurement set is obtained by a-priori selecting all the frequencies which will be used in the measurement session and by building a table of M_s values for all the amplifier gains and frequencies.

The impedance uncertainty depends on several factors, but three main uncertainty sources can be highlighted.

- Standard resistor uncertainty. This contribution depends on the uncertainty calibration of the resistor and on its drift and is expected to be negligible with respect to the other uncertainty contributions.
- Parasitic effects due to cables and connectors. This uncertainty contribution can be important when low capacitance and/or very high impedances have to be measured. The parasitic effects can be minimized by using shielded cables and partially corrected by a calibration process.
- Environmental noise. This kind of uncertainty can lead to severe problems especially when dealing with frequencies close to the power supply distribution frequency (50 Hz or 60 Hz depending on the country). A reduction of the environmental noise can be obtained by employing suitable shields, even though such a solution can be difficult to apply in the field. Alternately, a notch filter can be employed, even though this impairs the instrument capabilities near the notch frequency.

An example of the combined effect of these uncertainty sources in a practical case is shown in Section V.

IV. BLOCK DIAGRAM OF THE PROPOSED EIS SYSTEM

The block diagram of the EIS system and the structure of the test cell are shown in Fig. 2, while a photograph of part of the prototype is shown in Fig. 3. The EIS system is based on a cheap digital signal processor (DSP) board by Texas Instrument. The board, which is referred to as TMS320C30 DSK, is conceived as a “starting kit” for teaching digital signal processors and contains a floating point processor (TMS320C30 DSP), a parallel port, which is used to connect the DSK to a PC, and an analog interface circuit (AIC). The AIC is an integrated circuit, which contains a programmable ADC and a digital to analog converter (DAC). Both converters have a resolution of 14 bits and are designed to work at a maximum speed of 20 kHz, even though higher values can be employed although with higher uncertainties.

The DSK is provided with an expansion bus which has been used to connect a custom board to the DSP. Such a board contains a 32KWord backed-up static RAM, two DAC's, an LCD

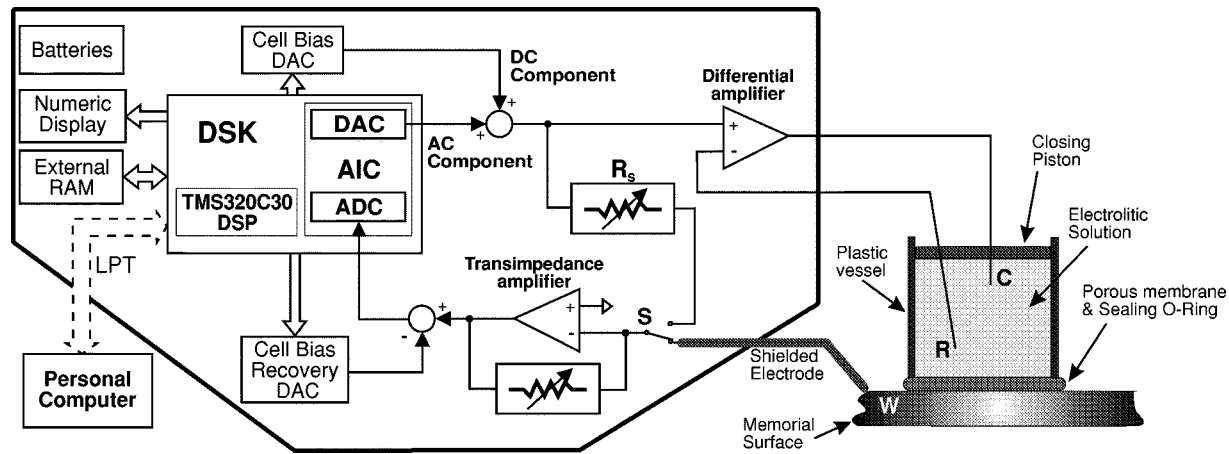


Fig. 2. Block diagram of the low-cost EIS system.

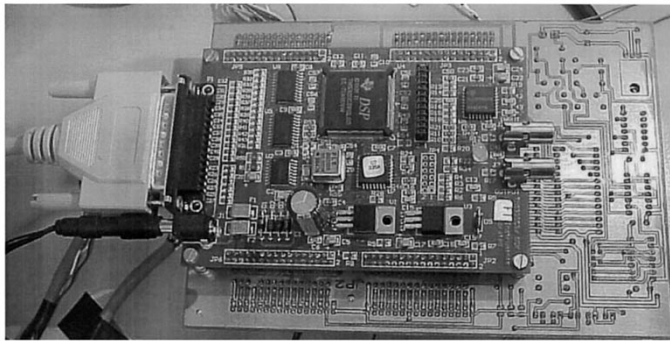


Fig. 3. Picture of the DSK and the RAM board.

display, the standard resistors, and some relays, which are used for configuring the input stages and the standard resistor values.

The DAC contained in the AIC is used to generate the stimulation sinusoidal voltage which is summed to the dc voltage produced by the Cell Bias DAC. The use of an external DAC for the bias generation allows the full AIC dynamic range to be employed, thus reducing the signal noise to very low values.

A differential amplifier is used to get rid of the voltage drop around the counter electrode, thus ensuring that the applied voltage is precisely present at the reference electrode.

The current, which flows through the cell or through the standard resistor, is converted into a voltage by means of the transimpedance amplifier and then sampled by the ADC. Such amplifier is designed to deliver transimpedances in the range of 10^5 V/A– 10^{11} V/A in six steps and embeds a notch filter tuned at 50 Hz. A set of standard resistors switched by means of relays permits to perform the calibration of the amplifier gains.

The cell bias recovery DAC is used to get rid of the dc components due to both the cell dc current and offset and bias of the transimpedance amplifier. This allows the ac current component to be amplified in order to use the complete AIC dynamic range. Such an ac component is eventually sampled by means of the AIC analog to digital converter.

The DSP performs the impedance measurement according to a time-domain algorithm, which is described in the Appendix, and drives the LCD to show a pass-fail result. All the computed impedances are stored in the backed-up RAM and can be read by a PC through a parallel port.

Measurements for frequencies in the range of 0.1 Hz–7 kHz and for impedances in the range of 1 k Ω –1 G Ω can be obtained. The measurement of higher impedances is possible up to 10 G Ω although at reduced accuracy.

The test cell is composed of a plastic vessel which is filled with an electrolytic solution. The vessel is closed at the top side by a piston and at the bottom (sensitive) side by a porous membrane; a rubber O-ring is used to provide the sealing between the vessel and the memorial. A shielded electrode inserted into the solution acts as the reference electrode; the working electrode is the memorial surface while the counter electrode is positioned in the top section of the vessel near the closing piston.

V. EXPERIMENTAL RESULTS

A. Preliminary Characterization

The preliminary EIS system characterization consists in the estimation of the parasitic shunt impedance which is present in the absence of devices connected to the input terminals. The measurement has been carried out by connecting together the counter and reference electrodes while leaving isolated the working electrode. The expected impedance is well above the values for which the EIS system is designed so that a large instability is expected in the measurements. For this reason several measurements have been averaged until stable traces have been obtained. The impedance values have eventually been used to determine the residual capacitance and shunt resistance by means of a least square approach. A residual equivalent capacitance of about 6 pF and a shunt resistance of about 15 G Ω have been obtained.

B. Simulated Cell

The performance of the EIS system has been tested by means of known electric networks that have been employed in the place of the three-electrode cell. Capacitors in the range of 330 pF–33 nF has been connected between the Reference (R) and Working (W) electrodes in order to simulate a good coating and experimental tests have been performed in the frequency range of about 0.1 Hz–7 kHz. Fig. 4 summarizes the instrument performance for different frequencies and impedance values. The uncertainty is generally confined within 4% for the module

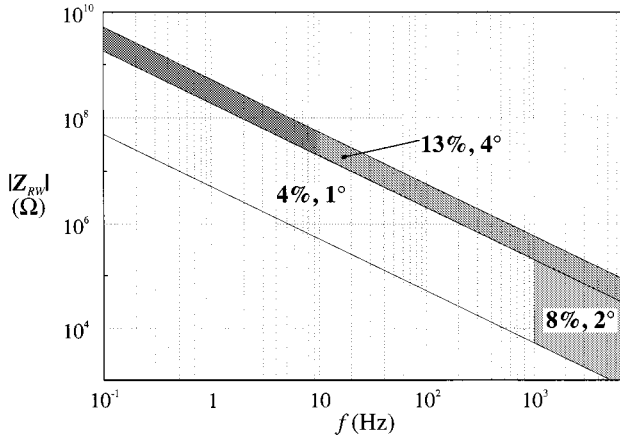


Fig. 4. Expected uncertainty performance of the EIS system.

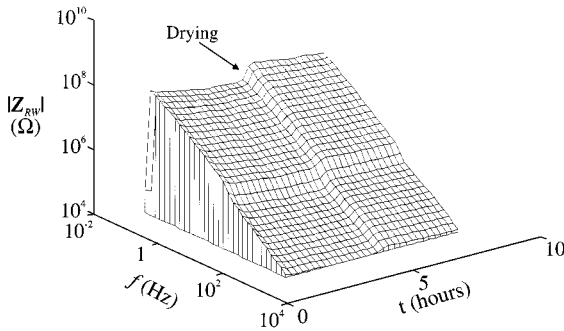


Fig. 5. Summary of a series of measurement on a water-based coating.

and 1° for the phase and increases up to 13% and 4° , for high impedance values and high frequencies.

Most of the uncertainty is a consequence of some small resonance effects, that are due to the very high employed gains. Such effects could be corrected by means of a suitable model, which is now under development.

C. An Example of Measurements with a Real Cell

The EIS system has been eventually used to measure the properties of different coatings. Fig. 5 shows one of the results obtained during a long measuring session on a water-based coating, which absorbs the humidity and therefore has an impedance which decreases as the time passes.

The figure shows a three-dimensional plot of the impedance versus frequency and time. It is easy to observe the capacitive nature of the coating and its degradation due to the absorbed solution. The plot also shows that the degradation is reversible as a drying process, applied after 5 h, restores the original impedance values.

VI. CONCLUSION

An EIS system has been presented which can be used to monitor the coating status of works of art and antiquities. The proposed instrument is based on a commercial DSP board and has a very limited cost in comparison to other commercial EIS systems. It is battery operated and thus completely portable, even though an interface allows the measured data to be downloaded into a conventional PC to perform more complex analyzes and

data display. It can measure impedances up to $1 \text{ G}\Omega$ with an uncertainty of about 4% maximum on the module and of about 1° on the phase. Such values can increase, depending on the amount of electromagnetic noise, when the instrument is used in the field, but the notch filter embedded into the instrument allowed the authors to perform meaningful measurements in all the tested conditions.

Most of the uncertainty is due to some systematic effects that can be corrected by means of a model, which is under development. If this systematic effects are removed, the uncertainty decreases below 0.1% and 0.1° for impedances of up to some megaohms.

APPENDIX ALGORITHM

Amplitude and phase estimation of sinusoidal signals can be obtained by expressing the acquired samples as:

$$S_i = S_0 + A_c \cos(ki) + A_s \sin(ki); \quad k = \frac{2\pi F_f}{F_s} \quad (4)$$

where S_i is the i -th sample of the signal, F_f is the signal frequency and F_s is the sampling frequency.

The equation contains four parameters (F_f , A_c , A_s , S_0), but the frequency is known since it is generated by a digital to analog converter, which shares the same clock of the sampling system. In addition, the synchronous nature of the acquisition allows an easy estimation of the offset S_0 , which can be obtained as the signal mean over an integral number of periods so that amplitude parameters A_c and A_s can eventually be estimated as

$$A_s = \frac{2}{n} \cdot \sum_{i=1}^n \sin(ik) \cdot (S_i - S_0) \quad (5)$$

$$A_c = \frac{2}{n} \cdot \sum_{i=1}^n \cos(ik) \cdot (S_i - S_0). \quad (6)$$

This algorithm can be performed without storing the samples, provided that the DSP is able to perform all the calculation within the sampling time, and allows a rough estimation of the result correctness to be easily obtained as

$$\|e_r\| = \frac{\sqrt{\sum_{i=1}^n (S_i - S_0)^2 - A_s^2 - A_c^2}}{\sqrt{\sum_{i=1}^n (S_i - S_0)^2}}. \quad (7)$$

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Prof. Spinelli is a member of the Working Party "Electrochemical Engineering" of the European Federation of Chemical Engineering and of the International Society of Electrochemistry, Italian Chemical Society, and Italian Association of Metallurgy.